

PATENT SPECIFICATION

930,132

F1

NO DRAWINGS.

Inventors :—GEORGE CECIL DAUL and THOMAS FRANCIS DRAKE.

Date of filing Complete Specification : Dec. 24, 1959.

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Index at Acceptance : —Classes 15(2), PA(1:6:12:17:18), PAX, PB2(A1:A2:B1:B2), PB5(A:B:C), PC1(F:H2A:H2X:H3A:H3X:L3), PC2A10, PC2A12(A4:A9:B1:B2:B4), PC2B3, PC2C(1:9:17); and 2(2), B2V(10:11).

International Classification :—D06m (D01f).

COMPLETE SPECIFICATION.

Improvements in the Treatment of Cellulose Textile Materials.

ERRATA

SPECIFICATION NO. 930,132

Page 2, line 7, for "aliphalic" read "aliphatic"

Page 4, line 46, for "fo" read "for"

Page 8, line 67

Page 9, line 8

after "1" insert "part"

THE PATENT OFFICE,
14th August, 1963

of the fibres and/or imparting various properties to the fibres, for example improved crease-resistance or dimensional stability in the case of a fabric comprising the fibres. For the purposes of the present specification, water-imbibition of a material means the per cent by weight of water remaining in a water-soaked sample of the material after centrifuging at 1000 G. for 5 minutes, expressed as a percentage of the weight of the bone-dry material. (Compare Journal of the Society of Dyers and Colourists, October 1948, page 331).

The literature abounds with descriptions of processes of the foregoing kind for effecting reaction between regenerated cellulose fibres and formaldehyde. A common recommendation is to impregnate the regenerated cellulose fibres with an aqueous solution of the formaldehyde and an acid-reacting substance and then to dry the material and heat it, for instance to a temperature above 100° C., during which drying and heating

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D 28796/1(4)/R.109 200 7/63 PL

following.

(1) The tensile strength of the fibres is often greatly reduced, probably due to the destructive action of the acid catalyst on the fibres.

(2) The effects lack uniformity; thus the treated material may dye irregularly and the water-imbibition of the treated fibres may vary from batch to batch although each batch has been given nominally the same treatment.

(3) The formaldehyde is incompletely utilised; a minor proportion only may combine with the cellulose, the remainder being lost during the drying and heating.

Clearly the reaction of formaldehyde with regenerated cellulose has been found very difficult to control. For instance attempts to get fuller utilisation of the formaldehyde by increasing the proportion of acid catalyst lead to increased destructive action on the fibres. For this reason the proportion of

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International Classification :—D06m (D01f).

COMPLETE SPECIFICATION.

Improvements in the Treatment of Cellulose Textile Materials.

We, LIPACO S.A., a corporation organised under the laws of the Canton of Basle, Switzerland, of 8 Elisabethenstrasse, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to the modification of textile fibres of cellulose by effecting the reaction of formaldehyde or other aldehydes therewith. It is more particularly concerned with effecting reaction between textile fibres of regenerated cellulose and an aldehyde for the purpose of reducing the water-imbibition of the fibres and/or imparting other desirable properties to the fibres, for example improved crease-resistance or dimensional stability in the case of a fabric comprising the fibres.

For the purposes of the present specification, water-imbibition of a material means the per cent by weight of water remaining in a water-soaked sample of the material after centrifuging at 1000 G. for 5 minutes, expressed as a percentage of the weight of the bone-dry material. (Compare Journal of the Society of Dyers and Colourists, October 1948, page 331).

The literature abounds with descriptions of processes of the foregoing kind for effecting reaction between regenerated cellulose fibres and formaldehyde. A common recommendation is to impregnate the regenerated cellulose fibres with an aqueous solution of the formaldehyde and an acid-reacting substance and then to dry the material and heat it, for instance to a temperature above 100° C., during which drying and heating the reaction with the fibres takes place. It appears that some of the more desirable results of the action of formaldehyde, for instance reduction of water-imbibition to a low value, can only be obtained by high temperature treatments of this kind. However, such treatments have been found exceedingly difficult to carry out satisfactorily in practice and, notwithstanding the demand for a means of reducing the water-imbibition of regenerated cellulose fibres and for improving the crease-resistance and dimensional stability of fabrics of regenerated cellulose fibres, the treatments have not been employed extensively. The reasons for this lack of commercial success include the following.

(1) The tensile strength of the fibres is often greatly reduced, probably due to the destructive action of the acid catalyst on the fibres.

(2) The effects lack uniformity; thus the treated material may dye irregularly and the water-imbibition of the treated fibres may vary from batch to batch although each batch has been given nominally the same treatment.

(3) The formaldehyde is incompletely utilised; a minor proportion only may combine with the cellulose, the remainder being lost during the drying and heating.

Clearly the reaction of formaldehyde with regenerated cellulose has been found very difficult to control. For instance attempts to get fuller utilisation of the formaldehyde by increasing the proportion of acid catalyst lead to increased destructive action on the fibres. For this reason the proportion of

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acid substance to formaldehyde recommended has usually been quite small.

According to the present invention the modification of cellulose textile fibres or regenerated cellulose fibres in paper form by reaction with formaldehyde or another aliphatic monoaldehyde or an aliphatic di- or polyaldehyde said aldehyde containing not more than 10 carbon atoms is effected by impregnating the fibres with an aqueous liquid containing the aldehyde, and a metal salt of a type defined below and then drying and heating the impregnated fibres, the molecular ratio of the salt to aldehyde in the liquid being at least 1 to 12.

In this way it is possible to secure exceptionally good and uniform utilisation of the formaldehyde. Further this very desirable result can be obtained without substantial loss in tenacity of the fibres. For instance, in the case of treating fabrics an important end result possible is the imparting of valuable properties such as reduced water-imbibition, improved crease resistance and improved dimensional stability while maintaining important mechanical properties, e.g. tensile strength and tear strength, at a higher level for a given reduction in water-imbibition, increase in crease-resistance or increase in dimensional stability, than has hitherto been regarded possible. This may be because the liquid containing formaldehyde need not be strongly acid and indeed may be at the most only faintly acid. It appears that the salt, employed in the proportion indicated, greatly restrains loss of formaldehyde (and consequently irregular loss of formaldehyde) during drying and heating.

In Patent Specification No. 504,916, an invention is described which, in one form, comprises simultaneously applying formaldehyde and a solution of zinc chloride to a cellulose textile material, partially drying the product and then subjecting it first to a pressing operation and then to a hot fixing operation. The proportions of zinc chloride to formaldehyde employed are far less than those which may be used in practising the present invention.

Patent Specification No. 455,472 discloses that textiles may be rendered crease-resistant by treatment with formaldehyde in the presence of "suitable catalysts", which include mercuric chloride. The molar proportions of salt to formaldehyde disclosed are again very small.

The metal salts employed in the present invention are salts of monobasic acids, especially inorganic acids, which would be ionised to the extent of at least 50 per cent if in normal aqueous solution at 18° C., for example hydrochloric acid, hydrobromic acid, hydriodic acid, nitric acid, perchloric acid, or thiocyanic acid. Further, the salts are salts in which the metal is bivalent and

belongs to Group II of the Mendeleeff Periodic Table of the elements, for example magnesium, beryllium, calcium, strontium, barium, zinc, and bivalent mercury.

The salt is preferably one of which the pH of a normal aqueous solution if not at least 5 can be brought to at least 5, by addition of sodium hydroxide, without precipitation of metal compound. This is true of the halides, nitrates and thiocyanates of magnesium, calcium, strontium and barium.

It is also advantageous to use salts which form hydrates which do not lose all their water when heated to 90° C. in air. Examples of such hydrate-forming salts are magnesium chloride, bromide, iodide and nitrate, calcium chloride, bromide, iodide, nitrate and thiocyanate, beryllium chloride, strontium chloride, barium chloride, magnesium perchlorate, and zinc nitrate.

Still another salt which may be used to assist the reaction of formaldehyde with regenerated cellulose is magnesium benzene sulphonate.

As the salt, magnesium chloride has been found particularly useful for the purposes of the invention. It is both cheap and particularly effective.

Preferably the ratio of magnesium chloride or other salt to the formaldehyde is from 1:12 to 1:4. Larger proportions may be used, though little advantage appears to be secured by exceeding a molecular proportion of 1:4. Very good results can be obtained by using 1 mol proportion of the salt to 6 mol proportions of formaldehyde; this corresponds to about equal weights of formaldehyde and magnesium chloride hexahydrate $MgCl_2 \cdot 6H_2O$.

As already indicated, the new process involves impregnating the regenerated cellulose fibres with an aqueous liquid containing the formaldehyde and magnesium chloride or other salt. The proportion of formaldehyde required on the material depends on the required degree of modification of the fibres and may be from 0.5 to 7 per cent or even up to 10 per cent of the dry weight thereof, particularly in the case of regenerated cellulose fibres. Since the maximum amount of liquid which can be incorporated in the fibres and retained reasonably uniformly therein during subsequent manipulation up to the drying stage is of the order of 100 per cent of the dry weight of the material, the aqueous treatment liquids may contain formaldehyde to the extent of 0.5 to 7 per cent by weight together with the magnesium chloride or other salt in the ratio referred to above.

The formaldehyde employed for the preparation of the treatment liquids can be in the form of the commercially available aqueous solutions; the latter may contain methyl alcohol. The formaldehyde solutions may

be brought to neutrality, for example by means of caustic soda, before being used for the preparation of the treatment liquids. Again the formaldehyde may be employed as para-formaldehyde; the latter dissolves readily in aqueous solutions of magnesium chloride.

The pH value of the solution is preferably not below 4 and is with advantage from 5 to 8. It is a great advantage of the new procedure that the pH value of the impregnation solution may be quite high, for example 8, without affecting materially the reaction of the formaldehyde with the cellulose. In the case of using magnesium chloride, for instance, the pH value of the solution may be varied from 5.3 (approximately the pH value due to a 4 per cent content of formaldehyde and 4 per cent of magnesium chloride hexahydrate) to 7.5 by addition of caustic soda, without significantly affecting the action of the solution. The pH value of the solution should not be so high as to lead to precipitation of metal compound.

The new process may be applied to regenerated cellulose fibres, particularly those produced by the viscose process, in various forms. Thus it may be applied to loose regenerated cellulose staple fibres, for example fibres which have never been dried. The fibres may be well wetted with a sufficiency of the aqueous solution containing the formaldehyde and metal salt and then squeezed or centrifuged until the required proportion of solution remains.

In the case of the "never-dried" regenerated cellulose fibres, the procedure of impregnation may be by squeezing the wet fibres until the water content is below the water-imbibition figure, wetting thoroughly with the aqueous treatment solution and again squeezing until the liquid content is below the water-imbibition figure. This procedure minimises migration of the treatment solution during drying and greatly facilitates obtaining a uniform product. The material so impregnated may then be dried at 30° to 110° C. and then cured at 110° C. to 160° C. for 30 to 3 minutes. Still higher temperatures may be employed.

Again, the new process may be applied to structures containing regenerated cellulose fibres. The structures may be woven or knitted textile fabrics, or textile fabrics or other kinds, for example the so-called non-woven fabrics, or even paper.

In the case of the textile fabrics containing regenerated cellulose fibres, conventional padding methods may be employed for the impregnation with the treatment liquids; drying and curing may be carried out under the conditions indicated above for loose staple fibres. The fabrics may be of various constructions; thus they may consist wholly

of regenerated cellulose fibres or in part of these fibres and in part of fibres of other kinds, for example cotton, or fibres of cellulose acetate (acetone soluble cellulose acetate or cellulose triacetate), or fibres of synthetic linear polymers, for example of polyamides, such as nylon 6 or nylon 66, or of polyesters, for example polyethylene terephthalate, or of addition polymers derived from acrylonitrile. The regenerated cellulose fibres in the fabrics may be in the form of staple fibres or of continuous filaments.

The treatment of the regenerated cellulose fibres, whether in the form of loose fibres or of fabrics or other structures, in accordance with the new process may be associated with a treatment with or incorporation of other modifying agents. Thus the formaldehyde solutions may include conventional textile finishing agents, for example softeners, lubricants or antistatic agents, and more particularly in the case of fabrics, agents for stiffening, hand-building or imparting water- or soil-repellency. The lubricants include silicone products. The water-repellency-imparting agents also include products which are silicones; the latter may be of the type which can be polymerised on the fibre by a heat treatment. It will be appreciated that any such agents must be compatible with the formaldehyde and metal salt.

The new method of effecting reaction between formaldehyde and regenerated cellulose fibres may also be applied to other fibres composed wholly or in part of cellulose. Thus it may be applied to fibres of natural cellulose, for example cotton or linen, or to fibres of cellulose acetate which have been superficially saponified to provide them with a surface skin of cellulose.

While the new procedure employing certain salts has been described with reference to the treatment of textile fibres of cellulose with formaldehyde it may be employed in the analogous treatment of textile fibres of cellulose with the other aliphatic aldehydes mentioned above, including such aldehydes as are liable to be lost by volatilisation during drying of an aqueous solution thereof on the material. Examples of aldehydes other than formaldehyde which may be used include glyoxal and glutaraldehyde and also hydroxy adipaldehyde and other aliphatic hydroxy aldehydes containing not more than 10 carbon atoms.

Regenerated cellulose fibres swell so much in aqueous sodium hydroxide solutions that they cannot be mercerised satisfactorily with such solutions. On the other hand by treating regenerated cellulose fibres in accordance with the invention it is possible to obtain fibres which are much less swelled by aqueous sodium hydroxide solutions and which can be mercerised satisfactorily.

A series of comparative experiments was carried out to illustrate the merit of magnesium chloride as the assistant in the reaction of never-dried regenerated cellulose staple fibre with formaldehyde and also to show the importance of the limit of at least 1 to 12 on the molar ratio of magnesium chloride to formaldehyde. Samples of the never-dried regenerated cellulose fibres were soaked for five minutes in an aqueous solution containing formaldehyde and magnesium chloride in the amounts indicated. The samples were then centrifuged at 1000 G. for 3 minutes, dried at 80° C. for 30 minutes, and cured at 160° C. for 6 minutes. The samples were then scoured for 1 hour in water at pH 8 and 95° to 100° C., and the water imbibition determined. The results are given in the following table :—

	Mol ratio of HCHO to MgCl ₂	0.0%	Water imbibition for a formaldehyde content of :—					
			0.5%	1.0%	1.5%	2.0%	3.0%	4.0%
	(1) —	100 (1)						
25	(2) 6 : 0.09		88	84	75	73	55	54 (2)
	(3) 6 : 0.178		90	75	74	72	59	50 (3)
	(4) 6 : 0.355		88	76	65	65	55 (4)	47
	(5) 6 : 0.71		83	64	63	56 (5)	47	40
	(6) 6 : 0.9		74	61	57 (6)	53	48	42
30	(7) 6 : 1		75	62	61	49 (7)	45	40
	(8) 6 : 1.07		76	64	55 (8)	48	41	40
	(9) 5 : 1			63		51 (9)	43	39
	(10) 4 : 1			58		44 (10)	41	36

Notes.—Dry tenacities in grams per denier :—

35	(1) 2.48	(2) 2.01	(3) 2.18	(4) 2.21	(5) 2.34
	(6) 2.39	(7) 2.48	(8) 2.15	(9) 2.25	(10) 2.05

It will be seen from the table that much greater reductions in water-imbibition are obtained when the higher proportions of magnesium chloride to formaldehyde of at least 1 to 12 are employed. Again, it will be noted that for a given reduction in water-imbibition, 2 or 3 times as much formaldehyde is required when the molecular ratio of formaldehyde to MgCl₂·6H₂O is 18 : 1 or greater than when the ratio is much less, for example 8.5 : 1 or less.

In footnotes to the table, figures are given for the dry tenacity (which was measured on single fibres) of one sample of fibre from each series of experiments at constant ratio of formaldehyde to magnesium chloride; the sample selected is that having a water-imbibition nearest to 50 per cent. It will be seen that for a given reduction in water-imbibition, the loss of tenacity, which is in any case small, is not materially affected by the ratio of formaldehyde to magnesium chloride.

A further series of experiments was carried out to show quantitatively the better utilisation of the formaldehyde when the molar ratio of formaldehyde to magnesium chloride is 12 to 1 or less.

Samples of viscose rayon staple fibre were soaked in water containing 6 per cent of formaldehyde (2 moles per 1,000 grams) and 0, 1.35, 4.07, 6.75 and 9.5 per cent respectively of magnesium chloride hexahydrate (all by weight on the total weight of the solution). The samples were then centrifuged until they retained approximately 100 per cent of their weight of liquid and dried under vacuum. Portions of the samples were then analysed for formaldehyde, as were other portions after curing for 6 minutes at 160° C. In making the analyses, the formaldehyde (free and combined) was stripped from the material by means of 12 N sulphuric acid and estimated by the chromotropic acid method. The results are shown in the table below.

Sample	MgCl ₂ ·6H ₂ O		Molar ratio of HCHO to MgCl ₂	Percentage of HCHO found		
	per cent	moles per litre		(1) dried only	(2) dried and cured	(2) — (1) × 100
1	0	0	—	4.4	2.7	61.4
2	1.35	0.067	6 : 0.20	4.1	2.5	61.0
3	4.07	0.2	6 : 0.6	3.9	3.0	76.9
4	6.75	0.33	6 : 0.99	4.0	3.4	85.0
5	9.5	0.47	6 : 1.41	4.2	3.8	90.5

It will be noted that the proportion of formaldehyde retained after curing, relative to that applied, is very much greater at a molar ratio $\text{HCHO} : \text{MgCl}_2$ of 6:0.6 (i.e. 10:1), than at 6:0.20 (i.e. 30:1); indeed the latter is slightly inferior to no magnesium chloride at all.

In order to show the effect of varying the pH value of the treatment solution, the following experiment was performed. A mixture of 108 grams of 37 per cent formaldehyde solution, 40 grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 852 grams of water was prepared. The molar ratio of formaldehyde to magnesium chloride was 6:0.9. This solution had a pH value of 5.3. A portion of it was used to treat never-dried regenerated cellulose staple fibre in the manner of the preceding experiments. Further portions were used similarly after bringing to pH 6.0, 6.5, 7.0 and 7.5 respectively. The water imbibition of the treated samples (after scouring) ranged from 43 to 46 per cent and so is substantially independent of the pH value of the treatment solution over the range indicated.

The invention is further illustrated by the following Examples, in which parts and percentages are by weight, unless stated otherwise.

EXAMPLE 1.

A blanket of freshly spun, never-dried viscose rayon fibre (textile grade) still in the gel state after spinning and having a water imbibition value (W.I.) of 145 per cent was squeezed between pressure rollers to a liquid retention of 100 per cent on the weight of the cellulose.

The squeezed blanket was then passed under a spray of an aqueous solution containing 1.5 per cent of formaldehyde (by weight), 1.25 per cent of magnesium chloride hexahydrate and 0.4 per cent of a polyglycol stearate finishing agent. The bath was adjusted to pH 6.4 with caustic soda solution. The formaldehyde used for the preparation of the treatment solution was a methanol solution containing 46 per cent by weight of formaldehyde.

The material was then squeezed in two stages, using a pressurised intermediate squeeze and a final heavy squeeze (600 pounds per linear inch) to a final liquid retention of about 100 per cent on the dry weight of cellulose.

The treating bath was recirculated and replenished by metering in a concentrated mixture of magnesium chloride hexahydrate and formaldehyde. Similarly, concentrated finishing agent was added to the bath at a rate sufficient to maintain a constant concentration in the bath.

The treated, squeezed fibre blanket was opened, laid down as a bed on a conveyor, passed through a drier at a temperature of 145° F. (63° C.) and then through a cure

zone at a temperature of 320° F. (160° C.). Dwell time in the cure zone was 7 minutes.

The fibre product had a W.I. of 57 per cent, dry tenacity of 2.38 grams per denier, wet tenacity of 1.69 grams per denier. One sample was scoured at pH 8 for 1 hour at the boil. W.I. was 50 per cent after this treatment.

Another sample was scoured at pH 4 for 1 hour at the boil. W.I. was 48 per cent after this treatment.

EXAMPLE 2.

An aqueous solution was prepared containing formaldehyde and magnesium bromide ($\text{MgBr}_2 \cdot 6\text{H}_2\text{O}$), the content of formaldehyde being 3 per cent and the mol ratio of $\text{HCHO} : \text{MgBr}_2 \cdot 6\text{H}_2\text{O}$ being 6:0.6. Never-dried viscose rayon staple fibre was soaked in the solution, centrifuged for 3 minutes at 1000 G., dried at 80° C. for 30 minutes and then cured at 160° C. for 6 minutes. After scouring and drying, the W.I. was 45 per cent. On decreasing the ratio of formaldehyde to magnesium bromide to 6:0.8, 6:1.0 and 6:1.2, the W.I. of the products were 44 per cent, 40 per cent and 39 per cent, respectively.

EXAMPLE 3.

Desized fabric woven from yarns spun from 3 denier viscose rayon staple fibre (60 warp yarns per inch and 50 weft yarns per inch) was padded with an aqueous solution containing 6 per cent by weight of formaldehyde and 6 per cent by weight of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, the padding being conducted so as to leave the fabric carrying about its own weight of the solution. The molecular ratio of formaldehyde to magnesium chloride is thus about 6:0.9. The fabric was then dried on a pin frame at 80° C. and cured at 160° C. for 8 minutes. The cured material was washed, rinsed and dried.

A sample of the damp treated material was pressed dry on a rotary ironer, conditioned and tested for wrinkle recovery on the Monsanto Wrinkle Recovery Tester and for tensile strength on 1 inch wide strips. The wrinkle recovery angle $W \div F$ was 292° and the tensile strength 56 pounds per inch. The corresponding figures for the original fabric were 226° and 62 pounds per inch.

Experiments were carried out in which the fabric used according to Example 3 was treated as in that Example, using solutions containing 6 per cent of formaldehyde but varying proportions of magnesium chloride. The results of tests on the treated fabrics are given in the following table which also includes a specimen of the fabric of Example 3. The wrinkle recovery angles are the sums of measurements in the directions of the warp and weft, respectively and are determined by the Monsanto method.

	Molar ratio of HCHO to MgCl ₂	Wrinkle recovery angle	Tensile strength pounds per inch
1	—	226°	62
2	6 : 0.09	206°	63
5 3	6 : 0.135	222°	71
4	6 : 0.178	226°	70
5	6 : 0.27	232°	64
6	6 : 0.45	266°*	60
7	6 : 0.675	278°	58
10 8	6 : 0.9	292°	56
9	6 : 1.0	288°	56

* It will be observed that there is a rapid increase in wrinkle recovery angle at this point, that is at about the point where the molar ratio of magnesium chloride to formaldehyde exceeds 1 to 12.

15

EXAMPLE 4.

Pieces of the same fabric as used in Example 3 were treated with various concentrations of a mixture of formaldehyde and magnesium chloride hexahydrate (6 : 1 mol ratio) with varying amounts of polyvinyl alcohol (stiffening agent), of an acrylic polymer emulsion, Rhoplex B-15 (40 per cent) (Rohm & Haas Co.) a hand-builder, and of a silicone emulsion, Sylsoft 10 (40 per cent) (Dow-Corning) a non-polymerisable lubricant. The pieces were padded with the respective treating solutions to 100 per cent

pick-up, dried on a pin frame at 80° C. and cured at 160° C. for 8 minutes. All the pieces were then washed with detergent. Samples of the materials were tested as follows.

Half of each sample was boiled in water for one hour, dried and pressed flat before testing.

Water imbibition and Monsanto Wrinkle Recovery tests were run on the samples before and after boiling. Results are shown below :—

40

	HCHO conc. %	MgCl ₂ · 6H ₂ O conc. %	PVA %	40% Acrylic Polymer emulsion %	40% Silicone emulsion %	Before boil : W.I. %	After boil : WRA °	After boil : W.I. %	After boil : WRA °
45	0	0	0	0	0	100	226	96	—
	3.3	3.7	0.24	0	2	38	258	39	252
	4.2	4.8	0.24	0	2	30	266	34	278
	5.2	5.9	0.24	0	2	30	274	33	272
	6.1	6.9	0.24	0	2	29	290	30	288
50	3.3	3.7	0.24	3.0	2	43	242	40	260
	4.2	4.8	0.24	3.0	2	41	252	42	256
	5.2	5.9	0.24	3.0	2	36	280	37	266
	6.1	6.9	0.24	3.0	2	31	284	34	286
	6.1	6.9	0.24	0	2	30	298	31	294
55	6.1	6.9	0.32	0	2	32	292	31	292
	6.1	6.9	0.40	0	2	30	292	31	296
	6.1	6.9	0.24	0	0	29	294	31	292
	6.1	6.9	0.32	0	0	31	288	31	288
	6.1	6.9	0.40	0	0	29	286	31	286
60	6.1	6.9	0	0	2	29	298	30	292
	6.1	6.9	0	0	4	28	292	32	288
	6.1	6.9	0	0	6	31	290	32	286

Selected samples from the above were scoured in water at pH 4 to simulate acid souring in a commercial laundry, rinsed in water, dried and retested. No measurable loss in wrinkle recovery properties was noted.

In each of the foregoing Examples 2 to 4, the pH value of the formaldehyde treatment liquor was if necessary brought to between 5 and 7 before using the liquor.

EXAMPLE 5.

Pieces of desized and bleached cotton fabric of the weave known as "Oxford" (98 warp yarns per inch and 47 weft yarns per inch) were treated with various concentrations of a mixture of formaldehyde and magnesium chloride hexahydrate (6 : 1 mole ratio), with 0.3 per cent of polyvinyl alcohol and 4 per cent of a 40 per cent silicone emul.

sion. The pieces were padded in the respective solutions to 100 per cent wet pick-up, placed on pin frames, dried at 80° C. and cured at 150° C. for 8 minutes. The

pieces were washed in detergent, dried and portions tested for wrinkle recovery (Montanto Method) and water imbibition. Results are shown below :—

	HCHO conc. %	MgCl ₂ .6H ₂ O conc. %	Water imbibition %	Wrinkle recovery angle °
10	0	0	44	170
	2.4	2.7	29	234
	3.3	3.7	29	238
15	4.2	4.8	28	254
	5.2	5.9	26	252
	6.1	6.9	26	256

EXAMPLE 6.

- A fabric of the following construction was processed :—
- 20 Weave—plain
Warp and weft—yarn of 1/32's cotton count spun from 1½ denier bright viscose rayon staple fibre of length 1⁷/₁₆ inches.
Warp yarns per inch—88; weft yarns per inch—60.
The fabric was padded with the following liquor so as to retain its own weight thereof.
- 25 Aqueous formaldehyde (40 per cent strength containing 7 to 8 per cent of methanol) 16 parts
Magnesium chloride crystals MgCl₂.6H₂O 6 parts
Silicone Emulsion (40 per cent a polymerisable silicone) 4 parts
Catalyst N 16 (a cobalt salt polymerisation catalyst for the
30 silicone) 0.8 part
Starch ether (solvitose H.D.F.)—a hydroxyethyl ether of starch 0.25 part
Water to make 100 parts by weight.

- The fabric was then dried on a pin stenter at 135° C. and cured for 5 minutes at 160° C.
- 35 It was then rinsed in hot water, washed off in a 2 gram per litre soap solution and dried on an overfeed pin stenter. The resulting fabric underwent negligible shrinkage when subjected to the machine wash shrinkage test (British Standard BS 1118) at 200° F. (93° C.)
- 40 whereas the original fabric shrunk about 10 per cent warp ways and 5 per cent weft ways under the same treatment. The water-imbibition of the treated fabric was about
- 45 36 per cent as against 100 per cent for the untreated fabric.

EXAMPLE 7.

- A fabric of the kind treated in Example 6 was padded with a preparation of the following composition so as to leave on the fabric about 80% of the composition based on the dry weight of the fabric :—
- 50 Glyoxal (30% aqueous solution) 3 parts
Magnesium chloride hexahydrate 1 part
55 "Mykon S.F." (Registered Trade Mark) (an aqueous dispersion of poly-ethylene) 1 part
60 Water to make 100 parts by weight

- The fabric was then dried at 120° C., heated at 150° C. for 5 minutes, washed in an aqueous soap solution, and dried. The treated fabric has a water imbibition of 42% and shrinks less than 2% warpways and weftways when washed at 60° C.
- EXAMPLE 8.
- Two woven fabrics were treated :—
- (A) A plain woven fabric of yarns spun from viscose rayon staple fibre, the fabric weighing about 4 oz. per square yard, and having about 78 warp yarns per inch and about 55 weft yarns per inch.
- (B) A gabardine fabric woven from yarns spun from viscose rayon staple fibre, the fabric weighing about 5 oz. per sq. yard and having about warp yarns per inch and 60 weft yarns per inch.
- Portions of the fabrics were padded with the following compositions :—

		Composition	
		A	B
Formaldehyde (calculated as HCHO)	5.34 parts	4.0 parts
MgCl ₂ .6H ₂ O	5.34 "	4.0 "
Quaker 40 (a polyacetal)	2.0 "	2.67 "
Silicone XLE—45	2.0 "	—
Cationic softener		0.8 "
Water to make	100	100

- The pH value of the compositions was pH 5.5 to 6. The padding (impregnation) was conducted in each case so as to leave on the fabric about 75% of composition calculated on the dry weight of the fabric. The fabrics were then dried at about 138° C. and then heated to 160° C. for about 3 minutes. The properties of the original and treated fabrics are given in the following table :—

Fabric	Treatment Composition	Water Imbibition after Washing	Elmendorf tear strength lbs.		Tensile strength (lbs. per inch)		Shrinkage after 5 washes at 71° C. per cent	
			Warp ways	Weft ways	Warp ways	Weft ways	Warp ways	Weft ways
A	none	100	2.2	1.8	55	53	- 20	- 1.1
A	A	36	3.4	3.2	41	44	- 1.6	- 0.8
A	B	40	2.9	2.8	51	58	- 2.0	- 0.9
B	none	105	4.0	3.0	107	53	- 25.3	+ 7.0
B	A	40	4.1	3.3	109	44	- 2.4	- 1.1
B	B	48	4.0	3.2	102	43	- 2.8	+ 0.5

The treated fabrics showed very good resistance to creasing.

EXAMPLE 9.

- A fabric having a warp of continuous filament viscose rayon yarns and a weft of viscose rayon staple fibre yarns was padded with the following composition so as to leave on the fabric about 85% of the composition based on the dry weight of the material.

		Parts by weight
Aqueous formaldehyde (400 g. per litre)	..	10
Magnesium chloride hexahydrate	4
Mykon S.F. (a polyethylene emulsion)	..	1
Elvano 72—60 (Polyvinyl alcohol)	..	0.2
Water to make	100

The fabric was dried first at 120° C. and then at 140—150° C. It was then baked at 165—170° C. for about 6 minutes.

The resulting fabric has a water-imbibition of 35 to 40 per cent and did not shrink more than 2% either warpways or weftways when submitted to the washing test of British Standard No. 1118. The original fabric had a water imbibition of about 100 per cent and shrunk about 10 per cent warpways and 5 per cent weftways when submitted to the same washing test.

EXAMPLE 10.

A regenerated cellulose fabric of the kind treated according to Example 6 was padded with the following composition so as to leave on the fabric about 90 per cent of the composition based on the dry weight of the fabric.

	Parts by weight	
Aqueous formaldehyde (400 g. per litre) ..	16	
5 Calcium chloride crystals (CaCl ₂ · 2 H ₂ O) ..	8	
Mykon S.F. (a polyethylene emulsion)	1	
Water to make ..	100	
10 The fabric was then dried at 120° C. and baked for 6 minutes at 160° C. As com- pared with the fabric before treatment, the fabric showed a greatly diminished change in dimensions when washed and had a greatly		normal aqueous solution at 18° C., the salt being one of which a normal aqueous solution can be brought to a pH of from 5 to 8 by addition of sodium hydroxide without pre- cipitation of metal compound, and the molecular ratio of metal salt to aldehyde being at least 1 to 12. 65
15 reduced water-imbibition.		4. Process according to Claim 2, wherein the metal salt is a magnesium halide. 70
		5. Process according to Claim 2, wherein the metal salt is magnesium chloride. 70
		6. Process according to Claim 4 or 5 wherein the molecular ratio of magnesium halide to formaldehyde is 1 to 6. 75
		7. Process according to any of Claims 2, 4, 5, and 6 wherein the cellulose fibres are of regenerated cellulose.
		8. Process according to Claim 7 wherein the regenerated cellulose fibres are impreg- nated with the formaldehyde and salt before they have ever been dried. 80
		9. Process according to Claim 8, wherein water-wet regenerated cellulose fibres which have never been dried are squeezed until the water content is below the water-imbibition figure, wetted thoroughly with the aqueous solution containing the formaldehyde and metal salt, and again squeezed until the water content is below the water-imbibition figure. 85
		10. Process according to Claim 7, wherein a textile fabric containing regenerated cellu- lose fibres is treated. 90
		11. Process according to any of Claims 2 and 4 to 10, wherein the proportion of formal- dehyde carried by the fibres at the time of drying is from 0.5 to 7 per cent based on the weight of the fibres. 95
		12. Process as claimed in Claim 1 for effecting reaction between cellulose textile fibres and formaldehyde, substantially as described in any of examples 1 to 6. 100
		13. Process for effecting reaction between cellulose textile fibres and formaldehyde, substantially as described in any of examples 8, 9 and 10. 105
		14. Process for effecting reaction between regenerated cellulose textile fibres and gly- oxal, substantially as described in Example 7.
		15. Processes according to Claim 1 for effecting reaction between cellulose textile fibres or regenerated cellulose fibres in paper form and an aldehyde, substantially as des- cribed. 110
		16. Cellulose textile fibres or regenerated cellulose fibres in paper form with which an aldehyde has been reacted by a process claimed in any of Claims 1 to 15. 115
WHAT WE CLAIM IS:—		
1. Process for modifying cellulose textile fibres or regenerated cellulose fibres in paper form by reaction with formaldehyde, or		
20 another aliphatic monoaldehyde or an aliph- atic di- or polyaldehyde said aldehyde con- taining not more than 10 carbon atoms, which comprises drying and heating the fibres after impregnation with an aqueous solution containing the aldehyde and a salt		
25 of a bivalent metal from Group II of the Mendeleeff Periodic Table with a monobasic acid, the acid being one which is ionised to the extent of at least 50 per cent when in normal aqueous solution at 18° C., and the molecular ratio of metal salt to aldehyde being at least 1 to 12.		
30 2. Process for modifying cellulose textile fibres by reaction with formaldehyde, which comprises drying and heating the fibres after impregnation with an aqueous solution of pH of from 5 to 8 containing the aldehyde and a salt of a bivalent metal from Group II of the Mendeleeff Periodic Table with a monobasic acid, the acid being one which is		
40 ionised to the extent of at least 50 per cent when in normal aqueous solution at 18° C., the salt being one of which a normal aqueous solution can be brought to a pH of from 5 to 8 by addition of sodium hydroxide without precipitation of metal compound, and the molecular ratio of metal salt to aldehyde being at least 1 to 12.		
45 3. Process for modifying cellulose textile fibres or regenerated cellulose fibres in paper form by reaction with an aliphatic di- or polyaldehyde or an aliphatic hydroxy alde- hyde said aldehyde containing not more than 10 carbon atoms, which comprises drying and heating the fibres after impregnation with an aqueous solution of pH value from 5 to 8 containing the aldehyde and a salt of a bivalent metal from Group II of the Mendeleeff Periodic Table with a monobasic acid, the acid being one which is ionised to the extent of at least 50 per cent when in		

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